SPECIFICATION:

Paragraph [0012] (Currently amended) There remains a need for analyte detectors and decontaminators that provide the specificity of biosensors and the benefit of ~~calorimetric~~ colorimetric sensors, but also provide the cost-efficiency, stability, accuracy, reliability, reproducibility, and robustness that is lacking from available technologies. In particular, development of devices that can be miniaturized with controlled shapes and that do not rely on an energy source and can be coated on a predetermined surface would also be very beneficial, particularly for routine fieldwork and home use.

Paragraph [0016] (Currently amended) FIG. 2 shows the ~~calorimetric~~ colorimetric detection of metal cations by EDTA-doped silica gels;

Paragraph [0024] (Currently amended) The sensor produces a ~~calorimetric~~ colorimetric change upon exposure of the sensor to a desired compound. The color change occurs immediately upon exposure of the sensor to a compound, thereby enabling the detection of a compound immediately without requiring lengthy exposure to the compound. The color change is preferably noticeable, thus eliminating the possibility of a false response. In other words, the color change is not subtle so as to prevent confusion as to whether or not exposure to the compound has occurred. The ~~calorimetric~~ colorimetric indicators of the present invention are agent-selective and specific to a sharp color change. Highly active chromophores contained in the indicators are specially designed to produce an intense color change that is visible in standard field lighting conditions while subjected to the presence of 0.01 g/m.sup.2 of a specific CWAs

and organophosphorus pesticides (or insecticides). The indicator's sensitivity is high and the response time to a specific color change is short. The indicators are low-cost and easy to use in field conditions by workers or soldiers who have only limited chemical knowledge. Preferably, the colorimetric indicators for detecting APs (or insecticides) and CWAs are metal-ligand complexes, enzymes, and pH indicators, which are encapsulated in sol-gel derived silica (or zirconia) monoliths, thin filmstrips, colloidal sols and aerosols.

Paragraph [0025] (Currently amended) By way of example, a set of seven ~~calorimetric~~ colorimetric indicators was fabricated for detecting the agricultural pesticides (APs), such as parathion, isophenfos, and diazinon, and chemical warfare agents (CWAs), such as HD (a blistering agent), VX (a "nerve" agent), GB (Sarin) and GD (Soman) "nerve" agents. The indicators were encapsulated in sol-gel derived silica (or zirconia) matrix and processed in the forms of monoliths, thin filmstrips, colloidal sols and aerosols. Examples of the indicators include, but are ~~riot~~ not limited to, an indicator with Cu (II), an indicator with a Lewis acid, Cu.sup.2+/PEDTA, CuZnSOD, Ni.sup.2+/dimethylglyoxime, thymol blue/Fichlor, thymol blue/sarinase, thymol blue/somanase, and thymol blue/parathion, hydrolase. The colorimetric indicators of APs and CWAs can also be fabricated in the forms of gel powder, colloidal sol and aerosol. Gel powder has a large active surface area, and it can act not only as a carrier, but also as an absorber. Moreover, the gel powder offers a better "blanket" coverage over the contaminated area, displays a higher sensitivity, and gives a safer detection and decontamination process. FIG. 3 illustrates a schematic diagram of an aerosol

reactor for producing gel powder. The silica and zirconia sols of ~~calorimetric~~ colorimetric indicators are pumped and sprayed via an ultrasonic atomizer. The temperature of the furnace can be adjusted to control the pore size of the silica and zirconia gel powders. The powder size can be controlled by the concentration and viscosity profiles of the sol. The colloidal sol is formed by dispersing gel powder into solvent (alcohol or water), and modified by using dispersion agent with a well-controlled pH. The fine gel powder is fluidized, which is easy to spray on the contaminated site by applying only a little pressure (similar to the air cleaner aerosol).

Paragraph [0035] (Currently amended) The present invention provides a family of seven colorimetric indicators and three heterogeneous catalysts encapsulated in silica and zirconia gels and for use in sensing and detoxifying APs and CWAs. The first objective was the fabrication and testing of these ~~calorimetric~~ colorimetric indicators. Effective ~~calorimetric~~ colorimetric indicators for the decontamination of APs (or insecticides) and CWAs can be sensitive and easy to use, and can have a fast time response. Moreover, the decontamination indicator can respond specifically to a selective APs and CWAs. The specificity of a colorimetric indicator to a selective APs and CWAs can depend on the chemical nature of both agents to be detected and their associated indicators. Table 1 lists seven ~~calorimetric~~ colorimetric indicators for detecting APs and CWAs and their color changes. Indicators (1) and (2) are based on the Lewis acid nature of Cu.sup.2+ chelated with a ligand, propylethylenediamine triacetate (PEDTA linked to the sol-gel matrix covalently) and a protein, bovine copper-zinc

superoxide dismutase (CuZnSOD), respectively. The sky blue color of Cu.sup.2+/PEDTA and blue-green color of CuZnSOD are resulted from the d-d transition of the Cu.sup.2+d.sup.9 metal ion. TABLE-US-00001 TABLE 1 Colorimetric Indicators for APs and CWAs Expected Indicator/ Color Zirconia Gel Type/Color Agent to be detected Change Cu.sup.2+/PEDTA A/Sky Blue HD Violet CuZnSOD B/Blue-Green HD Violet Ni.sup.2+/ C/Red VX Yellow Dimethylglyoxime (Green or Blue) Thymol blue/Fichlor D/Blue VX Yellow to Red Thymol blue/ D/Blue GB Yellow Sarinase to Red Thymol blue/ D/Blue GD Yellow Somanase to Red Thymol blue/ D/Blue Pesticides Yellow Parathion hydrolase (or Insecticides) to Red

Paragraph [0038] (Currently amended) The ~~calorimetric~~ colorimetric indicators are low cost (<$25 per indicator), have a short response time (<1 minute), and are environmentally friendly, easy to use, and portable. More importantly, the highly active chromophores contained in the indicators are specially designed to produce an intense color change that is visible in standard field lighting conditions while subjected to the presence of 0.01 g/m.sup.2 of a specific CWAs and organophosphorus pesticides (or insecticides). The heterogeneous catalysts, Ce.sup.4+/zirconia, Th.sup.4+/zirconia, and Zr.sup.4+/zirconia are expected to effectively and selectively speed up the rate of hydrolysis of APs and CWAs. The methods, materials, and tests are detailed below.

Paragraph [0047] (Currently amended) The ~~calorimetric~~ colorimetric indicators of APs and CWAs can also be fabricated in the forms of gel powder,

colloidal sol, and aerosol. Gel powder has a large active surface area, and it can act not only as a carrier, but also as an absorber. Moreover, the gel powder offers a better "blanket" coverage over the contaminated area, displays a higher sensitivity, and gives a safer detection and decontamination process. FIG. 3 illustrates a schematic diagram of an aerosol reactor for producing gel powder. The silica and zirconia sols of ~~calorimetric~~ colorimetric indicators are pumped and sprayed via an ultrasonic atomizer. The temperature of the furnace can be adjusted to control the pore size of the silica and zirconia gel powders. The powder size can be controlled by the concentration and viscosity profiles of the sol. The colloidal sol is formed by dispersing gel powder into solvent (alcohol or water), and modified by using dispersion agent with a well-controlled pH. The fine gel powder is fluidized and is easy to spray on the contaminated site by applying only a little pressure (similar to the air cleaner aerosol).

Paragraph [0052] (Currently amended) Colorimetric indicators for APs and CWAs are selective, specific, sensitive, easy to use and low cost. For the ~~calorimetric~~ colorimetric detection of metal cations, the chelating agent doped silica is capable of detecting the trace amount of heavy metal ions in the contaminated water (5 ppb) with a response time of 2 to 900 seconds. A universal ~~calorimetric~~ colorimetric indicator can be fabricated by mixing gel powders doped with two or more types of indicator compounds. The successful colorimetric indicators are expected to be low cost (<$25 per indicator), have short response time (<1 minutes), are environmentally friendly and easy to use, and portable (can be affixed on vehicles, equipment, uniforms of soldiers and

workers, and facilities). More importantly, the highly active chromophores are specially designed to produce an intense color change that is visible in standard field lighting conditions while it is subjected to the presence of 0.01 g/m.sup.2 of a specific CWAs and organophosphorus pesticides (or insecticides).

Paragraph [0053] (Currently amended) Zero leaching of M.sup.n+/PEDTA and CuZnSOD complexes out of the gel matrix. The leaching problem, occasionally encountered in sol-gel doping procedures, was solved by two methodologies: first, zirconia tetrapropoxide (or trimethoxyorthosilane) polymerization at high acidity and low water content; and second, doping with N-(trimethoxysilylpropyl) ethylene diamine triacetic acid, trisodium salt (TMSPEDTA) capable of forming a covalent bond within the encapsulating cage, resulting in the permanent anchoring of the dopant. The quality assurance, of the ~~calorimetric~~ colorimetric indicators and heterogeneous catalysts for APs and CWAs calls for zero leaching.

Paragraph [0055] (Currently amended) The commercialization of these revolutionary ~~calorimetric~~ colorimetric indicators and heterogeneous catalysts for chemical warfare agents and agricultural pesticides, (or insecticides) save lives not only on the battlefield and in agriculture, but also for the general public during the wartime and terrorist attacks. Fast, easy, and accurate identification of the deadly agents reduces the cost of the decontamination process and enhance the military's readiness.

Paragraph [0067] (Currently amended) Table 3 displays the orbital energy and orbital compositions (i.e., a linear combination of the extent of atomic orbitals

involved) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for some HD analogue compounds. Table 4 lists the calculated heat of formation (H.sub.f, in kcal/mol) for some HD analogue compounds and Cu(II)/HD analogue complexes. In Table 3, the chlorination of sulfide compounds gives a greater orbital stabilization (a more negative energy) of LUMO than HOMO. The MO contributions in the unchlorinated sulfides are mainly made up of sulfur and its attached carbon atom(s). However, the chlorinated HD analogue compounds show a large extent of contribution of chlorine atom(s) in the orbital formations, especially in the orbital compositions of LUMO. A charge-transfer between sulfur and chlorine atoms is evidence that the compounds can promote the formation, and then enhance the ~~calorimetric~~ colorimetric detection, of Cu(II)/HD analogue complexes in sol-gel sensors. The first two columns of Table 4 show an expected trend in the lowering of H.sub.f for the chlorine-substituted sulfide compounds. The last two columns of Table 4 give the following results: (1) Cu(H.sub.2O).sub.6 is highly stable as compared to other copper complexes, such as Cu(H.sub.2O).sub.2(CH.sub.3COO).sub.2, (2) the chlorinated HD analogue gives a stable Cu(II)/HD analogue complex, e.g., (H.sub.2O).sub.5Cu:S(C.sub.2H.sub.4Cl).sub.2(H.sub.2O).sub.5Cu:S(C.sub.2H-.sub.5)(C.sub.2H.sub.4Cl)>(H.sub.2O).sub.5Cu:S(C.sub.2H.sub.5).sub.2, and (3) the CT complexes formed in 1:1 ratio of Cu(II):HD analogue is about 30 kcal/mol lower in energy than those formed in 1:2 ratio, and is about 150 kcal/mol lower in energy than those formed in 1:4 ratio. So, a 1:1 complex of Cu(II)/HD analogue is

preferred. TABLE-US-00003 TABLE 3 Energies and compositions of HOMO and LUMO for HD analogue Orbital compositions HD analogue Orbital energies (in eV) HOMO LUMO CH.sub.3--S--CH.sub.2CH.sub.3 LUMO 0.4086 Sp.sub.y 0.9312 Sp.sub.x 0.6359 HOMO -8.8694 C1p.sub.y -0.1374 C1p.sub.z 0.3547 C2p.sub.y -0.1403 C2p.sub.z -0.3165 C3p.sub.y -0.0130 C3p.sub.z 0.0754 CH.sub.3CH.sub.2--S--CH.sub.2CH.sub.3 LUMO 0.4222 Sp.sub.y -0.7068 Sp.sub.x 0.5677 HOMO -8.9872 C1p.sub.z 0.0775 C1p.sub.x -0.3766 C2p.sub.y 0.0774 C2p.sub.x 0.3437 C3p.sub.x 0.1145 C3p.sub.x -0.0419 C4p.sub.y -0.1121 C4p.sub.x -0.0321 CH.sub.3--S--CH.sub.2Cl LUMO -0.1180 Sp.sub.y -0.9290 Sp.sub.x 0.6068 HOMO -9.1541 C1p.sub.y 0.1405 C1p.sub.z 0.3316 C2p.sub.y 0.1366 C2p.sub.z 0.4155 C1p.sub.y -0.0499 C1p.sub.z 0.3054 CH.sub.3--S--CH.sub.2CH.sub.2Cl LUMO -0.0256 Sp.sub.y 0.9301 Sp.sub.x -0.5789 HOMO -9.1231 C1p.sub.y -0.1409 C1p.sub.z -0.2721 C2p.sub.y -0.1421 C2p.sub.z -0.3308 C3p.sub.y -0.0197 C3p.sub.x -0.1701 C1p.sub.y -0.0499 C1p.sub.z -0.2515 CH.sub.3CH.sub.2--S--CH.sub.2CH.sub.2Cl LUMO -0.0437 Sp.sub.y 0.7727 Sp.sub.x -0.5136 HOMO -9.2630 C1p.sub.y -0.0784 C1p.sub.z 0.3998 C2p.sub.y -0.0847 C2p.sub.z -0.2784 C3p.sub.y 0.0870 C3p.sub.y -0.0283 C4p.sub.y 0.1307 C4p.sub.z 0.1591 C1p.sub.y -0.0737 C1p.sub.z 0.1737 ClCH.sub.2CH.sub.2--S--CH.sub.2CH.sub.2Cl LUMO -0.1755 Sp.sub.y 0.7766 Sp.sub.x -0.5848 HOMO -9.4299 C1p.sub.y -0.0893 C1p.sub.z 0.3632 C2p.sub.y -0.0918 C2p.sub.x -0.3278 C3p.sub.z -0.1071 C3p.sub.z 0.0453 C4p.sub.y 0.1379 C4p.sub.z 0.1175 C11p.sub.y -0.0915 C11p.sub.z 0.1385 C12p.sub.z 0.0438 C12p.sub.y 0.0185